SPECTRAL TRANSMITTANCE OF SINGLE CRYSTAL AMMONIUM PERCHLORATE AND DEUTERATED AMMONIUM PERCHLORATE

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FOREWORD

Ammonium perchlorate is the oxidizer and principal ingredient in many solid propellants. This report, which describes the spectral transmittance of single crystal ammonium perchlorate and deuterated ammonium perchlorate, is part of a larger effort concerned with ignition and combustion phenomena of solid propellants.

The report was reviewed for technical accuracy by Allen L. Olsen and Thomas L. Boggs.

The work was performed under Naval Weapons Center Independent Research funds, Project Number R00001, Task Area Number R01301.

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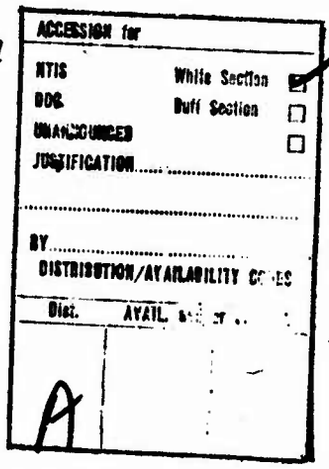

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(U) *Spectral Transmittance of Single Crystal Ammonium Perchlorate and Deuterated Ammonium Perchlorate*, by Marian E. Hills and William R. McBride. China Lake, Calif., NWC, August 1974. 8 pp. (NWC TP 5683, publication UNCLASSIFIED.)

(U) The spectral transmittance of large single crystals of ammonium perchlorate and deuterated ammonium perchlorate grown from aqueous solution has been measured in the ultraviolet, visible, near infrared, and infrared regions of the spectrum. The crystals are transparent in the visible and throughout much of the ultraviolet. The absorption edge of both the deuterated and undeuterated crystals lies in the ultraviolet region near 200 nanometers. There are strong absorption bands in the near infrared and infrared regions. The intensity of an absorption band at 1.55 micrometers was used to estimate the mole percent hydrogen in deuterated ammonium perchlorate cyrstals.

INTRODUCTION

Ammonium perchlorate (NH_4ClO_4) is widely used as an oxidizer in solid propellants. Although it has been studied extensively, [1,2] little information about its spectral transmittance, particularly in the 0.16 to 2.5 micrometer (μm) range, is available. Such information would be helpful, for example, in estimating the effectiveness of radiation of a given wavelength in heating a crystal for decomposition studies.

Large single crystals of ammonium perchlorate up to several centimeters on an edge were grown from aqueous solution by a temperature lowering technique.[3] Ammonium perchlorate, ultra high purity grade, from American Potash and Chemical Corporation was used to prepare the solutions from which the crystals were grown.[4] At room temperature ammonium perchlorate is orthorhombic and has cleavage planes parallel to the *m* (210) and *c* (001) faces.[5]

Deuterated ammonium perchlorate (ND_4ClO_4) was prepared by successive recrystallizations, from deuterium oxide, of ammonium perchlorate purchased from Apache Chemicals Inc. The deuterium oxide (99.85 mole percent D_2O) was obtained from Bio-Rad Laboratories. Single crystals of deuterated ammonium perchlorate were grown from a deuterium oxide solution by the temperature-lowering technique. The crystals have the same habit and cleavage as the undeuterated crystals.

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[1]Hall, A. R., and G. S. Pearson. "Ammonium Perchlorate as an Oxidizer," OXIDATION AND COMBUST REV, Vol. 3, No. 2 (March 1968), pp. 129-239.

[2]Jacobs, P. W. M., and H. M. Whitehead. "Decomposition and Combustion of Ammonium Perchlorate," CHEM REV, Vol. 69, No. 4 (August 1969), pp. 551-90.

[3]McBride, W. R., "Solution Growth of Ammonium Perchlorate Crystals," *American Committee for Crystal Growth Conference on Crystal Growth*, National Bureau of Standards, Gaithersburg, Md., 12 August 1969.

[4]Boggs, T. L., E. E. Petersen, and D. M. Watt, Jr. "Comment on 'The Deflagration of Single Crystals of Ammonium Perchlorate'," COMBUST AND FLAME, Vol. 19, No. 1 (August 1972), pp. 131-33.

[5]Tutton, A. E. H. "The Alkali Perchlorates and a New Principle Concerning the Measurement of Space-Lattice Cells," *Proceedings of the Royal Society (London)*, Vol. A111, No. A758 (June 1926), pp. 462-91.

The results of studies on the decomposition and deflagration of the ammonium perchlorate crystals have been reported by Boggs and co-workers.[6] Comparable studies of the deflagration of deuterated ammonium perchlorate crystals are in progress. Elsewhere (Picatinny Arsenal and National Bureau of Standards), Raman spectroscopy and neutron diffraction are being employed to characterize both the ammonium perchlorate and the deuterated ammonium perchlorate crystals. The present work deals with the spectral transmittance of the crystals.

AMMONIUM PERCHLORATE

The absorption spectra in the ultraviolet, visible, and near infrared were measured with a Cary Model 14 spectrophotometer with light incident upon an *m* (210) face of the crystal. Ammonium perchlorate is transparent in the visible and throughout much of the ultraviolet. The absorption edge lies in the vicinity of 200 nanometers (nm), in agreement with the value of 204 nm given by Maycock and Pai Verneker.[7] A value of about 300 nm reported earlier by Galwey and Jacobs[8] may have been determined on specimens having high scattering losses.

To determine that the strong absorption near 200 nm was the absorption edge and not the long wavelength side of an impurity band a few measurements were made in the far ultraviolet region. The transmittance of a crystal about 0.5 mm thick measured over the wavelength range 165 nm to 225 nm with a Beckman Model DK far ultraviolet spectrophotometer was essentially zero between 165 nm and 183 nm. The transmittance of a piece about 2 mm thick measured over the wavelength range 160 nm to 300 nm with a vacuum ultraviolet spectrometer was essentially zero between 160 nm and 189 nm. The 2 mm thick piece showed an absorption band near 265 nm; this band was not found in crystals measured on other instruments. Maycock and Pai Verneker[9] reported the formation of color centers in ammonium

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[6]Boggs, T. L., K. J. Kraeutle, and D. E. Zurn. "Decomposition, Pyrolysis, and Deflagration of Pure and Isomorphously Doped Ammonium Perchlorate," AMER INST AERONAUT ASTRONAUT J, Vol. 10, No. 1 (January 1972), pp. 15-16.

[7]Maycock, J. N., and V. R. Pai Verneker. "Role of Point Defects in the Thermal Decomposition of Ammonium Perchlorate," *Proceedings of the Royal Society (London)*, Vol. A307, No. 1490 (November 1968), pp. 303-15.

[8]Galwey, A. K., and P. W. M. Jacobs. "The Thermal Decomposition of Ammonium Perchlorate at Low Temperatures," *Proceedings of the Royal Society (London)*, Vol. A254, No. 1279 (March 1960), pp. 455-69.

[9]Maycock, J. N., and V. R. Pai Verneker. "Ultraviolet Photon Induced Color Centers in Ammonium Perchlorate," SOLID STATE COMMUN, Vol. 7, No. 14 (July 1969), pp. 979-81.

perchlorate upon ultraviolet irradiation of the crystal in a vacuum; however, none of the bands was at 265 nm. Nevostruev and co-workers[10] found bands at 260, 290, and 369 nm upon irradiation with 4.7 Mev protons.

The near infrared spectrum (Figure 1, Curve B) shows two strong bands near 1.55 and 2.1 μm and two weak bands near 1.05 and 1.26 μm (Figure 1, Curve C). Some of the bands have structure which is, for the most part, unresolved at room temperature. Single crystal potassium perchlorate does not absorb in the near infrared region and hence comparison of its spectrum with that of ammonium perchlorate indicates that the near infrared absorption of ammonium perchlorate is associated with the ammonium ion.

In the infrared region the absorption bands are so intense that it has not been possible to cleave crystal sections thin enough to bring the entire spectrum on scale. Curve B of Figure 2 shows the infrared spectrum measured on a Perkin-Elmer Model 221 spectrophotometer with an NaCl prism while Curve A shows the effect of the crystal holder alone on the 100% transmittance line of the instrument. The spectrum of ammonium perchlorate in mulls has been studied by a number of investigators including, recently, van Rensburg and Schutte.[11] They reported bands at 3.06, 7.07, 9.40, 10.70, and 16.00 μm and a shoulder at 15.77 μm at room temperature.

DEUTERATED AMMONIUM PERCHLORATE

The absorption spectra of deuterated ammonium perchlorate crystals in the ultraviolet, visible, and near infrared regions were measured with a Cary Model 14 or 14R spectrophotometer with light incident upon an *m* (210) face. The crystals are transparent in the visible and throughout much of the ultraviolet. The absorption edge lies in the vicinity of 200 nm. The near infrared spectrum (Figure 3, Curve A) shows a strong absorption band near 2.1 μm. The presence of an absorption band near 1.55 μm (Figure 3, Curve B) seems to indicate that not all of the hydrogen in NH_4ClO_4 has been replaced by deuterium. In order to obtain an estimate of the amount of hydrogen in the deuterated ammonium perchlorate it was assumed that all the absorption at 1.55 μm in deuterated ammonium perchlorate arises from hydrogen impurity and that the intensity of the band bears the same relationship to the hydrogen content for both ammonium perchlorate and deuterated ammonium perchlorate. By this

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[10]Nevostruev, V. A., L. T. Bugaenko, and Yu. A. Zakharov. "Radiolysis of NH_4ClO_4," CHEM ABSTR, Vol. 67 (1967), p. 8138.

[11]Van Rensburg, D. J. J., and C. J. H. Schutte. "Low-Temperature Infrared and Raman Studies, XI. The Vibrational Behaviour of Ammonium Perchlorate--Its Phase Changes and the Rotational Freedom of Its Ions," J MOL STRUC, Vol. 11, No. 2 (February 1972), pp. 229-39.

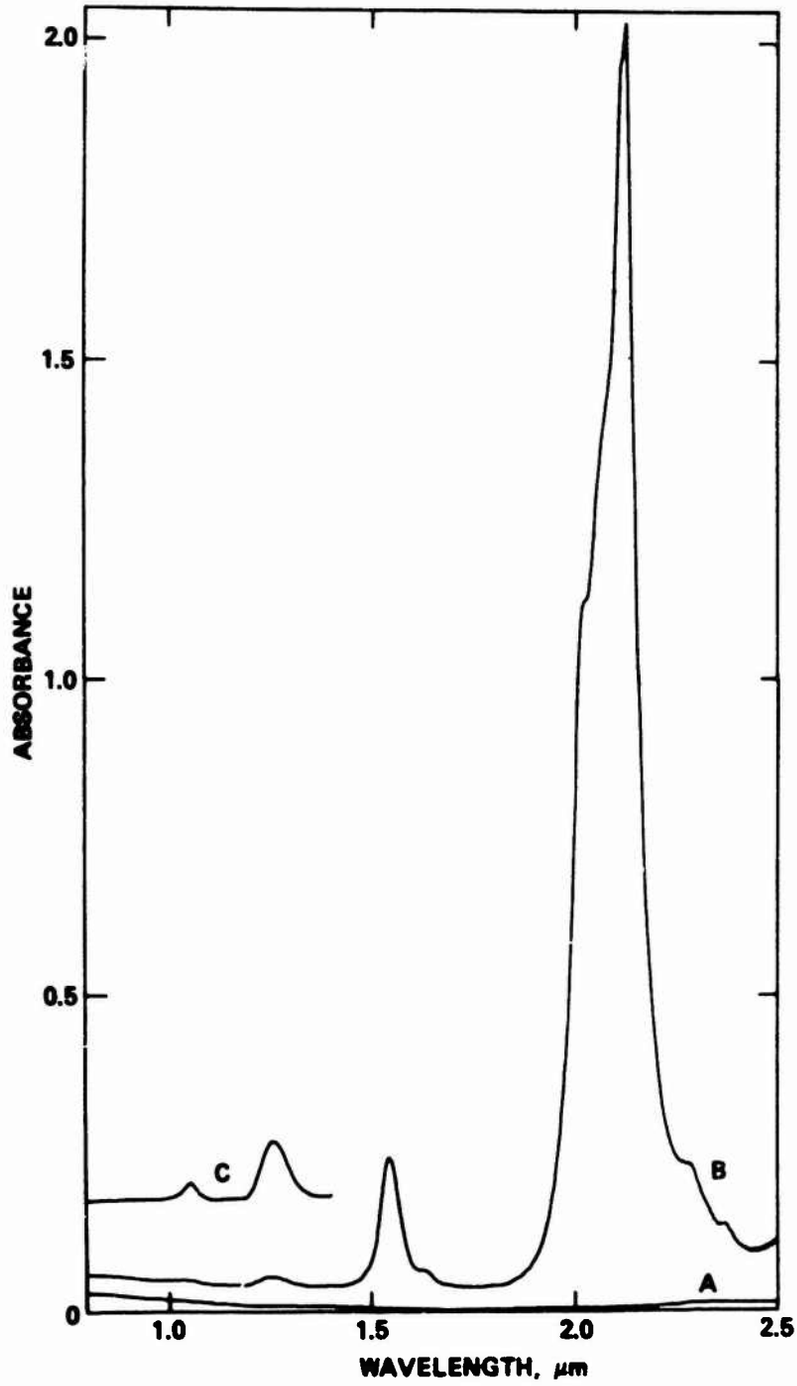

FIGURE 1. Near-Infrared Absorption Spectrum of Single Crystal Ammonium Perchlorate (not Corrected for Reflection Losses). Curve A: absorbance due to crystal holder. Curve B: crystal - 0.24 mm thick. Curve C: crystal - 0.96 mm thick (ordinate arbitrarily displaced; measurements with a different crystal holder).

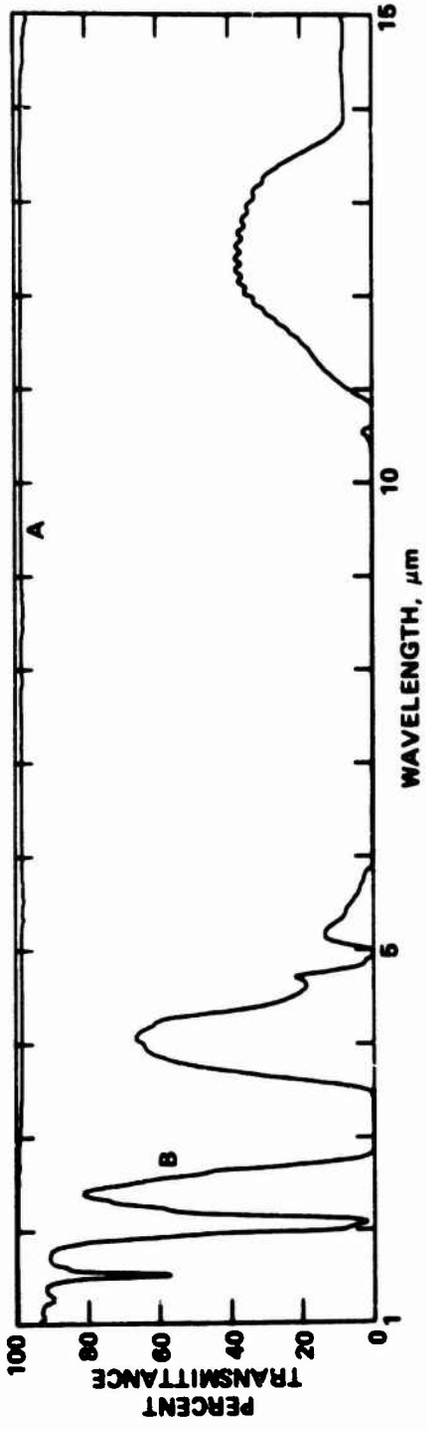

FIGURE 2. Infrared Transmittance Spectrum of Single Crystal Ammonium Perchlorate. Curve A: transmittance of crystal holder; Curve B: transmittance of crystal - 0.24 mm thick.

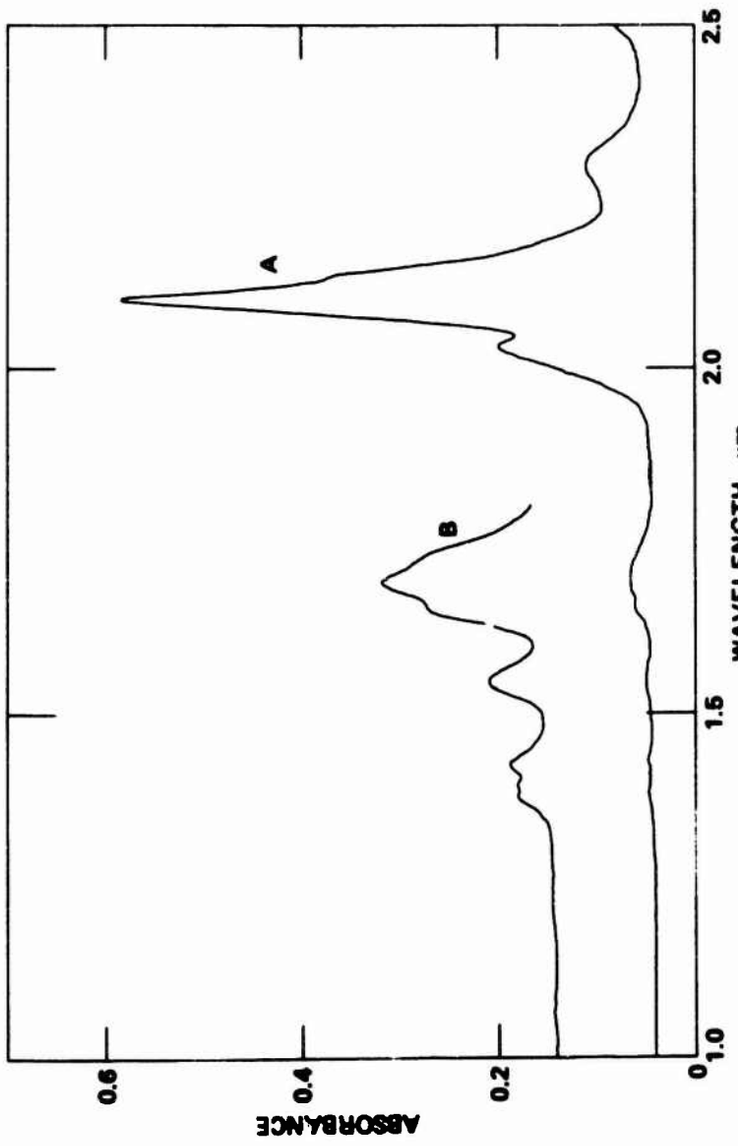

FIGURE 3. Near-Infrared Absorption Spectrum of Single Crystal Deuterated Ammonium Perchlorate (not Corrected for Reflection Losses). Curve A: crystal - 0.75 mm thick; Curve B: crystal - 5.30 mm thick (ordinate arbitrarily displaced).

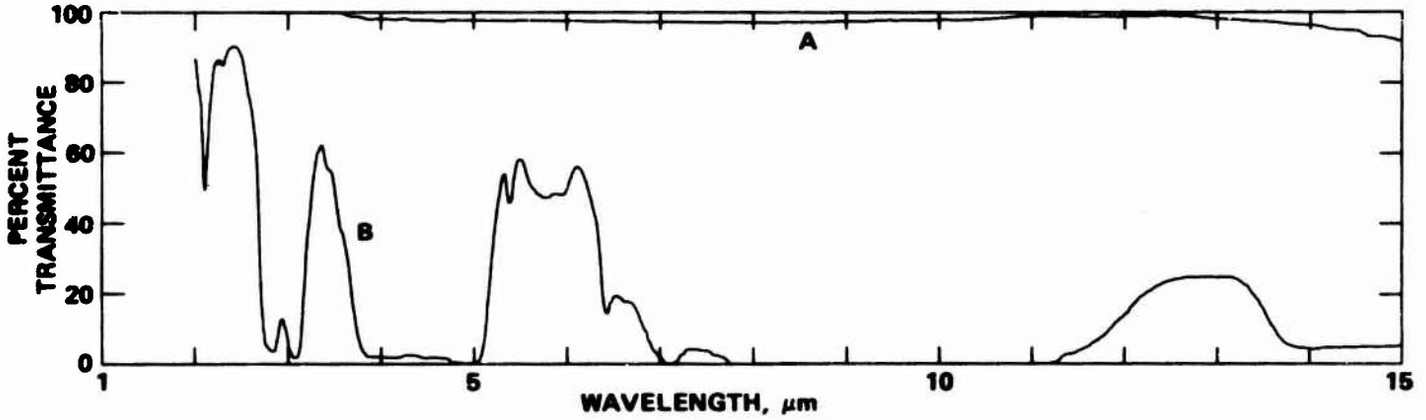

FIGURE 4. Infrared Transmittance Spectrum of Single Crystal Deuterated Ammonium Perchlorate. Curve A: transmittance of crystal mount. Curve B: transmittance of crystal - 0.40 mm thick.

procedure it was calculated that the deuterated ammonium perchlorate single crystal specimens contain 1.1 mole percent hydrogen. This result is confirmed generally by nuclear magnetic resonance techniques which established a value of 99.0 ± 1.0 mole percent deuterium in the deuterated ammonium perchlorate crystals.

The infrared spectrum (Figure 4) was measured with the light incident upon an *m* face. Curve B shows the spectrum of a crystal 0.40 mm thick while Curve A shows the effect of the crystal holder on the 100% transmittance line of the instrument. Van Rensburg and Schutte[11] reported bands at 4.07, 9.45, 10.70, and 16.05 μm at room temperature for deuterated ammonium perchlorate in mulls.

SUMMARY

The spectral transmittance of large single crystals of ammonium perchlorate and deuterated ammonium perchlorate grown from aqueous solution has been measured in the ultraviolet, visible, near infrared, and infrared regions of the spectrum. The crystals are transparent in the visible and throughout much of the ultraviolet. The absorption edge of both the deuterated and undeuterated crystals lies in the ultraviolet region near 200 nm. There are strong absorption bands in the near infrared and infrared regions. From the intensity of an absorption band at 1.55 μm the mole percent hydrogen in the deuterated ammonium perchlorate crystals was estimated to be 1.1.

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